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March 1, 1972 to August 31, 1972

SENSITIVITY FUNDAMENTALS

By: M. E. HILL, T. MILL, D. S. ROSS, R. SHAW, and R. W. WOOLFOLK

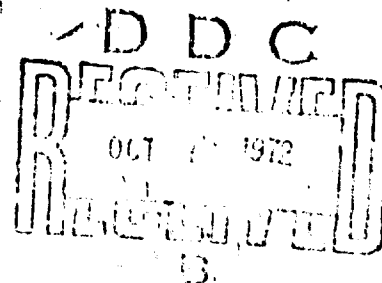
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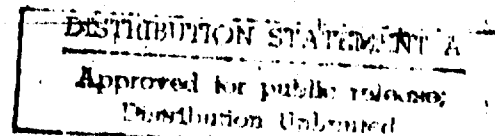
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13. ABSTRACT This report summarizes a six-month period of research on the relationship between detonation phenomena, chemical structure, and kinetics for isomeric dinitropropanes and other nitroalkanes, sponsored by the Office of Naval Research. Research on dinitropropanes is being carried out in three areas: high velocity detonation (HVD), low velocity detonation (LVD), and static high pressure and kinetic effects. Smooth-shock reaction times measurements on 1,1-DNE, 1,1,1-FDNE, 1,1-DNP, and 2,2-DNP confirm previous findings that at constant preshock temperature the shock pressure required to produce a specific reaction time is greater when there is no hydrogen-atom alpha to the nitro group and when an additional methylene group is present. The largest contribution to the variation of failure diameter with initial temperature is the variation in smooth-shock reaction time. Comparison of LVD and HVD gap sensitivities for 1,1-DNE and 1,1,1-FDNE shows that fluorine decreases HVD but not LVD sensitivity. Pressure-time measurements in LVD-initiated FEFO gave 4-7 kbar peak pressure and 3mm/ μ sec propagation velocity. FDNE fits the correlation of $\Delta H_f/\Delta H_v$ with LVD gap sensitivity. Thermal decomposition of 1,1-DNP at 1 atm and 1800 atm and 155°C gave 1-3% decomposition in 39 hrs but significantly different decomposition products including CH_3NO_2 , CO_2 , and N_2 at 1 atm. and two unidentified products and no CH_3NO_2 at 1800 atm.			

KEY WORDS	LINK A		LINK B		LINK C	
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Approved by:

M. E. HILL, *Director*
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Physical Sciences Division

PREFACE

This project is the responsibility of the Chemistry Laboratory's Physical Organic Chemistry Group in the Physical Sciences Division of Stanford Research Institute. Project organization and principal contributors to the technical work are:

Program Manager:	M. E. Hill
Project Supervisor:	T. Mill
Low-Velocity Detonation:	R. W. Woolfolk
Physics and Chemistry of Detonation:	R. Shaw
Static High-Pressure and Kinetic Effects:	D. S. Ross R. Shaw

SUMMARY

Physics and Chemistry of Detonation

Smooth-shock reaction time measurements on 1,1-DNE, 1,1,1-FNDE, 1,1-DNP, and 2,2-DNP confirm previous findings that at constant preshock temperature the shock pressure required to produce a specific reaction time is greater when there is no hydrogen-atom alpha to the nitro group and when an additional methylene group is present.

Following previous work by Dremin and Trofimov and by Enig and Petrone, we have shown analytically that the largest contribution to the variation of failure diameter with initial temperature is the variation in smooth-shock reaction time.

In collaboration with M. C. Lin of Naval Research Laboratory, we have calculated, using RRKM theory, that the rate constant for elimination of HF from 1,2-bis(difluoramino)propane is $\log (k/\text{sec}^{-1}) = 13.1 - (38.0/2.3 \text{ RT})$.

Low-Velocity Detonation (LVD)

We have found that for 1,1-DNE an increase in the temperature from 25° to 60°C causes a slight decrease in the LVD gap sensitivity. This behavior is in contrast to that for high velocity detonation (HVD) where increasing the temperature increases the HVD gap sensitivity.

The HVD and LVD gap sensitivity of 1,1,1-FDNE was determined and compared with that of 1,1-DNE. Substitution of a fluorine atom for a hydrogen atom caused the HVD gap sensitivity to decrease, but the LVD gap sensitivity remained nearly unchanged.

The results of the LVD tests on 1,1,1-PDNE were in agreement with the previously suggested correlation between LVD gap sensitivity and the ratio $\Delta H_r / \Delta H_v$, where ΔH_r is the heat of reaction and ΔH_v is the heat of vaporization. However, these same results did not agree with the relationship of oxygen balance to LVD gap sensitivity.

Pressure-time measurements in LVD-initiated FEFO showed a peak pressure in the range of 4-7 kbar and a velocity of propagation of 3.0 mm/ μ sec. Piezoresistive gages of ytterbium were placed in the explosive liquid to measure these pressures and velocities.

Static High-Pressure Experiments

We have designed a system to measure gross rates of reactions and initial products formed during the initiation period at pressures and temperatures comparable to those found in shock initiation experiments.

Initial experiments on thermal decomposition of 1,1-DNP in the liquid phase were done at 155°C and 1 atm pressure in glass as benchmark experiments. The products include N_2O , CO_2 , CH_3NO_2 , and an unknown organic material in amounts indicating 1-3% decomposition of 1,1-DNP in 39 hrs. This rate is about 20 times faster than that calculated from gas-phase data and, along with the product composition, suggests that free radical chain steps may be involved. Several static high pressure experiments were attempted with 1,1-DNP. However, the original design gave difficulties in product isolation.

An experiment with 1,1-DNP at 155° and 1.8 kbar (1800 atm) in Teflon tubing was complicated by loss of gaseous products and possible surface effects. Two new unknown products were found but no CH_3NO_2 .

Publications

Several manuscripts based on this program, have been completed during this period on dehydrofluorination of 1,2-DP, kinetics of decomposition of nitroalkanes (both theoretical and experimental), pyrolysis of 1,2- and 2,2-DP, shock initiation of nitromethane and methyl nitrite and a universal Hugoniot for liquids.

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GLOSSARY OF COMPOUNDS

Code Name

1,1-DNP	$\text{CH}_3\text{CH}_2\text{CH}(\text{NO}_2)_2$	1,1-dinitropropane
2,2-DNP	$\text{CH}_3\text{C}(\text{NO}_2)_2\text{CH}_3$	2,2-dinitropropane
1,2-DNP	$\text{CH}_3\text{CH}(\text{NO}_2)\text{CH}_2\text{NO}_2$	1,2-dinitropropane
1,1-DNE	$\text{CH}_3\text{CH}(\text{NO}_2)_2$	1,1-dinitroethane
EN	$\text{CH}_3\text{CH}_2\text{ONO}_2$	ethyl nitrate
1,1,1-FDNE	$\text{FC}(\text{NO}_2)_2\text{CH}_3$	1,1,1-fluorodinitroethane
1,1,1-FDNP	$\text{FC}(\text{NO}_2)_2\text{CH}_2\text{CH}_3$	1,1,1-fluorodinitropropane
1,2-DP	$\text{CH}_3\text{CH}(\text{NF}_2)\text{CH}_2\text{NF}_2$	1,2-bis(difluoramino)propane
2,2-DP	$\text{CH}_3\text{C}(\text{NF}_2)_2\text{CH}_3$	2,2-bis(difluoramino)propane
IBA	$(\text{CH}_3)_2\text{C}(\text{NF}_2)\text{CH}_2\text{NF}_2$	1,2-bis(difluoroamino)-2-methylpropane
NM	CH_3NO_2	nitromethane
FEFO	$[\text{F}(\text{NO}_2)\text{CCH}_2\text{O}]_2\text{CH}_2$	fluorodinitroethyl formal

I INTRODUCTION

Under the sponsorship of the Office of Naval Research (ONR), Stanford Research Institute is studying the fundamental sensitivity properties of liquid high-energy materials in order to define the minimum number of physical and chemical parameters of the system needed to predict detonation sensitivity. In this work we are now concerned primarily with: (1) detonability of the liquid phase, i.e., whether it will support a detonation wave, and the failure diameter for detonation; (2) the physical and chemical factors that affect detonation initiation and (3) the kinetics and chemistry of decomposition at very high pressures and high temperatures and their relationship with detonability.

In previous work on this contract,* these relationships were studied with isomeric difluoraminopropanes and butanes, and we are now studying nitro compounds in the analogous isomeric propane series and some ethane homologs. Thus a direct comparison between the two high-energy groups that are of most interest at present can be made, and basic knowledge can be obtained on the initiation and propagation properties of model liquid nitroaliphatic plasticizers.

This program consists of three primary tasks;

A. Physics and Chemistry of Detonation

The ultimate objective of studies of the physics and chemistry of detonation (Section II) is to correlate transient detonation phenomena, such as shock initiation and failure behavior, with the mode of decom-

* Stanford Research Institute Project 4051, Final Report, "Sensitivity Fundamentals," May 15, 1970.

position. This objective involves: (1) measurement of failure diameters, (2) study of events in the liquids as shocks of various magnitudes enter, and (3) measurement, evaluation, and correlation of physical and thermochemical properties.

B. Low-Velocity Detonation

The objectives of this program (Section III) are to determine under which conditions LVD will initiate and to relate this initiation to the chemical and physical properties of the materials. By comparing two classes of materials (i.e., the difluoramino and dinitro compounds) with such widely different thermochemical and kinetic properties, we can ascertain those factors that influence LVD initiation.

C. Static High-Pressure and Kinetic Effects

Section IV of this research effort comprises a study of the decomposition behavior of shock-sensitive liquids at very low and very high pressures including measurements of reaction times at pressures and temperatures comparable to those encountered in initiating shocks; and attempts to describe a relationship between detonation phenomena and chemical mechanism, including the elementary rate steps.

II PHYSICS AND CHEMISTRY OF DETONATION

(Robert Shaw)

A. Introduction

The objective of this part of the research program is to develop and test models for calculating the transient detonation properties of explosive liquids from their chemical structure. The transient detonation properties with which we are most concerned are initiation and failure of HVD, which is Chapman-Jouget (i.e., high-velocity) detonation. During the present report period we have performed a series of experiments on the shock initiation of dinitroalkanes, have completed the calculation of kinetics of decomposition of dinitroalkanes and vibrationally excited 1,2-bis(difluoramino)propane, and have begun a program to test Dremen's theory of detonation failure.

B. Shock Initiation

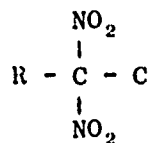
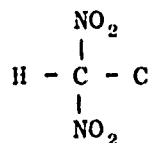
Preliminary results in the previous semiannual report¹ showed the existence of interesting correlations of shock initiation with chemical structure in the dinitroalkanes series. During the present report period we have extended these experiments (see Table I) and have confirmed the earlier findings of a methylene effect and an active alpha-hydrogen effect.

Table I

SMOOTH-SHOCK REACTION TIMES FOR NITROALKANES
MEASURED DURING THIS REPORT PERIOD

Compound	Preshock Temperature (°C)	Peak Pressure in Liquid (kbar)	Reaction Time (μ sec)
1,1-DNE	25	87	1.77
1,1-DNE	25	84	2.44
1,1-DNP	60	95	1.24
1,1-DNP	60	88	1.93
2,2-DNP	60	105	Failed (>4)
1,1,1-FDNE	25	104	1.21
1,1,1-FDNE	25	101	1.83

The methylene effect is illustrated in Figure 1 by comparing the shock initiation of 1,1-DNE with the next member of the homologous series 1,1-DNP. At a preshock temperature of 25°C, the shock pressure required to give a 1-μ sec reaction time for 1,1-DNE is some 10 kbar less than that for 1,1-DNP. The active α-hydrogen effect is observed when comparing two compounds of similar structure, one of which has a hydrogen alpha to the dinitro carbon and the other does not:



R ≠ H

α-hydrogen

no α-hydrogen

In propane series:

1,1-DNP

2,2-DNP

In ethane series:

1,1-DNE

1,1,1-FDNE

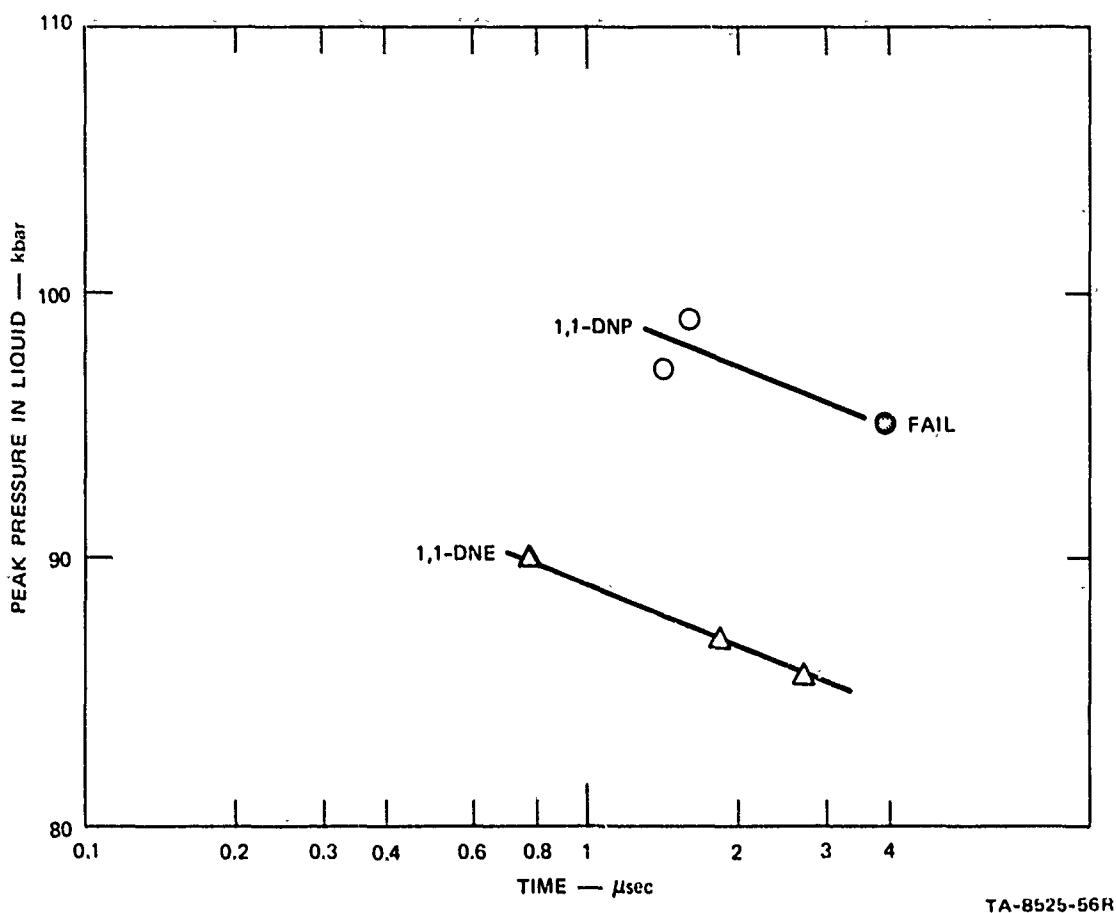


FIGURE 1 SMOOTH-SHOCK REACTION TIME MEASUREMENTS FOR 1,1-DNE AND 1,1-DNP AT A PRESOCK TEMPERATURE OF 25° C

Specifically, in Figure 2, comparison of the shock initiation of 1,1-DNP and 2,2-DNP (at a preshock temperature of 60°C, because 2,2-DNP is solid at 25°C) shows that the peak shock pressure in the liquid required to produce a 1-μ sec reaction time in 1,1-DNP is 94 ± 2 kbar, whereas for 2,2-DNP the corresponding shock pressure is greater than 105 kbar. We have found 2,2-DNP to be less sensitive to shock initiation than any compound studied on the entire project. We have not yet been able to initiate it, even with a 105-kbar shock at 60°C. We plan to measure its failure diameter to determine if that is the problem.

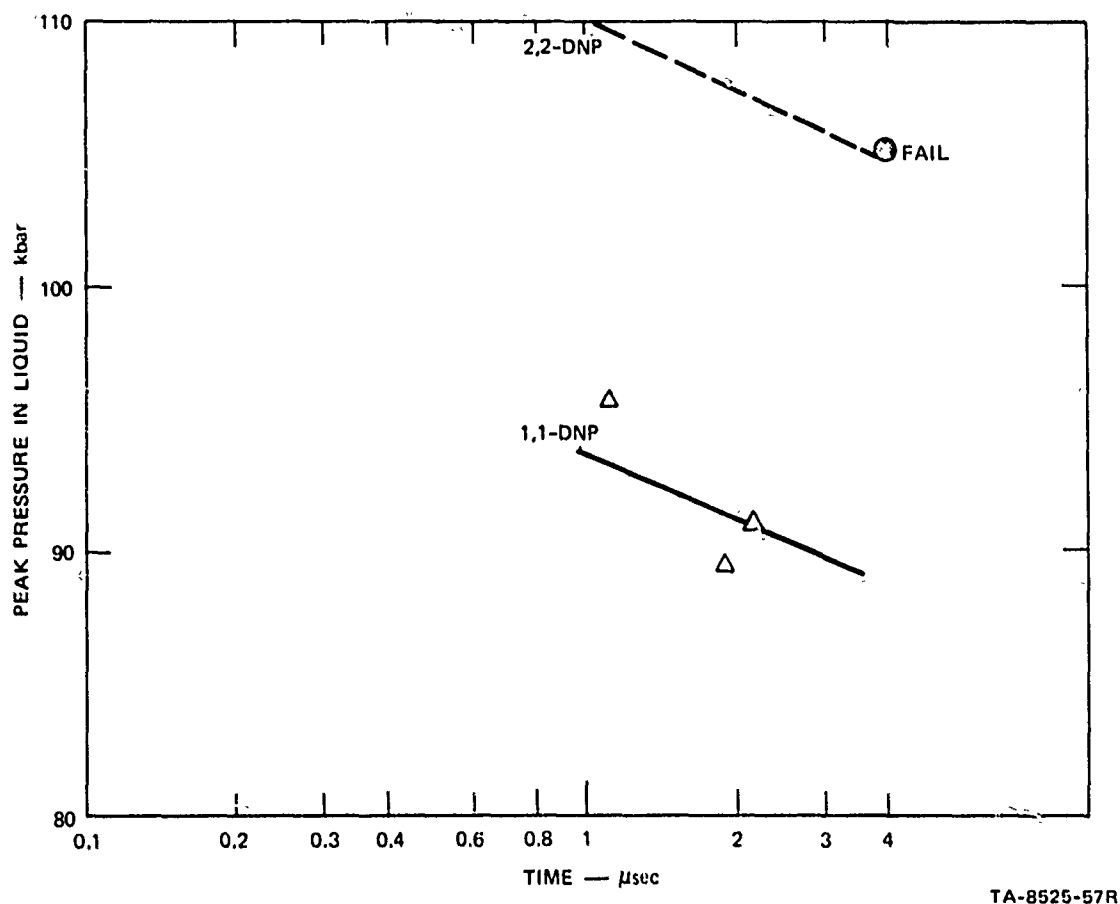


FIGURE 2 SMOOTH-SHOCK REACTION TIME MEASUREMENTS FOR 1,1-DNP AND 2,2-DNP AT A PRESOCK TEMPERATURE OF 60° C

Similarly, in Figure 3, comparison of 1,1-DNE and 1,1,1-FDNE at a preshock temperature of 25°C shows that the peak shock pressure in the liquid required to produce a 1-μ sec reaction time in 1,1-DNE is 89 ± 2 kbar, whereas for 1,1,1-FDNE the corresponding shock pressure is 102 ± 2 kbar.

Although we are not yet able to determine the detailed mechanism of the active alpha-hydrogen effect, we consider that the effect is unlikely to be due to differences in thermochemical and gas-phase kinetic

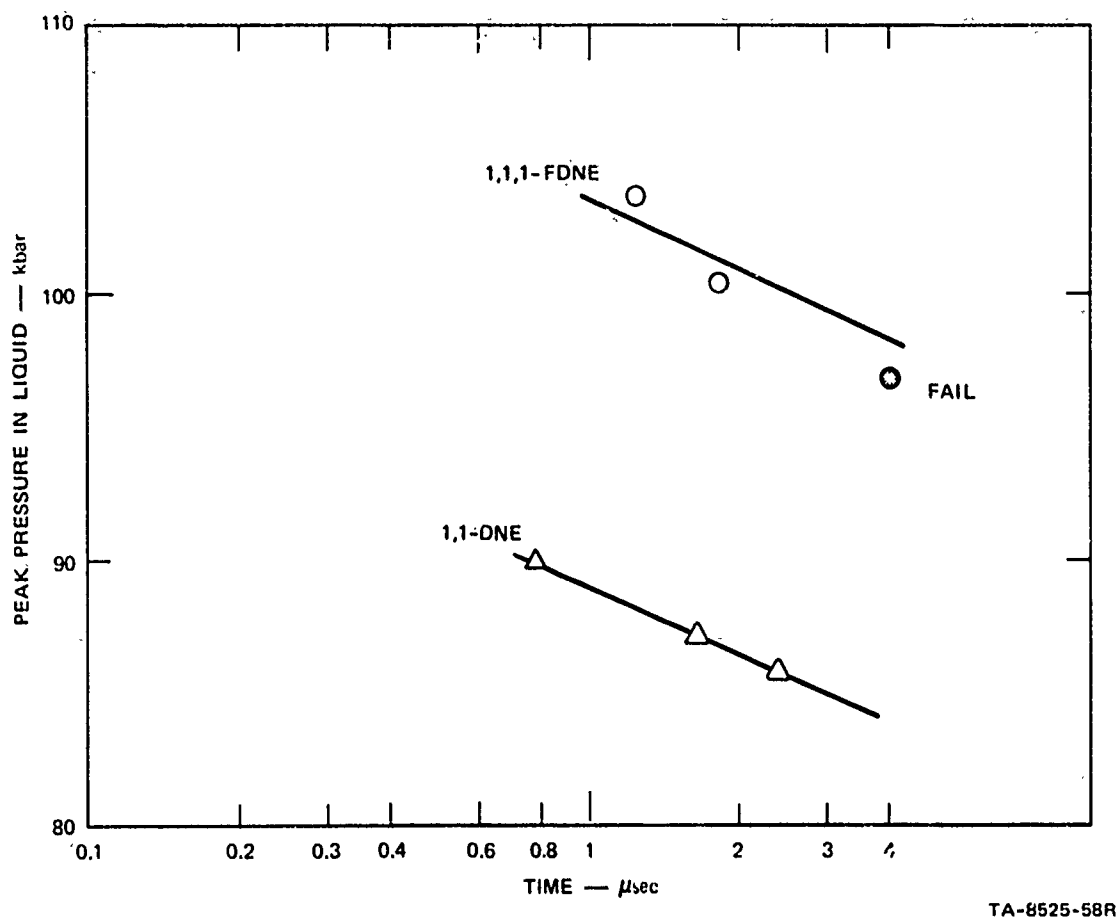


FIGURE 3 SMOOTH-SHOCK REACTION TIME MEASUREMENTS FOR 1,1-DNE AND 1,1,1-FDNE AT A PRESOCK TEMPERATURE OF 25° C

parameters. This is illustrated by comparing the properties of 1,1-DNP and 2,2-DNP in Table II.

The lack of correlation between initiation properties and strengths of the C-N bonds is also clearly shown by comparing 2,2-DNP and 1,2-DNP. The C-N bond strength in 2,2-DNP is 49 kcal/mole, which is some 10 kcal/mole weaker than the C-N bond strength in 1,2-DNP, which is close to 59 kcal/mole. Yet the temperature for a 100-second explosion time at 10 kbar is 230°C for 2,2-DNP, and 180°C for 1,2-DNP.

Table II

COMPARISON OF THERMOCHEMICAL AND KINETIC PARAMETERS (GAS-PHASE)
WITH LIQUID-PHASE INITIATION OF 1,1-, 2,2- and 1,2-DNP

Dinitroalkane	1,1-DNP	2,2-DNP	1,2-DNP	Ref.
Structure	$\text{CH}(\text{NO}_2)_2\text{CH}_2\text{CH}_3$	$\text{CH}_3\text{C}(\text{NO}_2)_2\text{CH}_3$	$\text{CH}_2(\text{NO}_2)\text{CH}(\text{NO}_2)\text{CH}_3$	
ΔH_f° /(kcal/mole)	-39.9	-43.3	-52.3	2
E /(kcal/mole) = $D(\text{C-N})$	49	49	59	3
$\log_{10}(A/\text{sec}^{-1})$ for C-N bond fission (assigned)	17.5	17.5	17.5	3
Temperature ($^\circ\text{C}$) for 50% decomposition in VJPP reactor	480	465	640	3
Peak shock pressure (kbar) re- quired to give 1- μsec reaction (at preshock temperature of 60°C)	93	103	--	3
Temperature ($^\circ\text{C}$) at 10 kbar static pressure required to give thermal explosion time of 10 sec	180	280	--	4
Temperature ($^\circ\text{C}$) at 10 kbar static pressure required to give thermal explosion time of 100 sec	--	230	180	4

C. Calculated Kinetics and Thermochemistry of Decomposition

Knowledge of kinetics and thermochemistry of decomposition is needed for the quantitative application of thermal explosion theory that is fundamental to our treatment of transient detonation phenomena.

In a previous report³ we discussed the thermochemistry of dinitroalkanes in terms of group additivity. Since then we have calculated kinetics of decomposition of dinitroalkanes from the known thermochemistry, transition state theory, and some key experiments by D. S. Ross and L. Piskiewicz. A paper on the results has been accepted for publication by the International Journal of Chemical Kinetics.² Since copies of the preprint were sent to ONR and to laboratories known to be interested in this research, this work is only summarized here.

Heats of formation of solid, liquid, and gaseous nitroalkanes were shown mostly to obey group additivity. Group values were obtained for carbon atoms attached to one, two, and three nitro groups. The heat of formation of 1,1,1,3,5,5,5-heptanitropentane, either solid or liquid, cannot be fitted to the scheme, even allowing for gauche effects. The differences between observed and estimated values for 1,1,1-fluorodinitroalkanes and 1,2-dinitroethane are larger than expected and should be investigated further.

Activation energies were calculated for decomposition by five-center elimination of HONO from mononitroalkanes and dinitroalkanes using thermochemistry and estimated activation energies for the reverse reactions. The key data for these estimates were previously reported^{5,6} activation energies for the decomposition of nitroethane and 1,2-dinitropropane. The calculations also gave values for the heats of formation (in kcal mole⁻¹) of nitroethylene 12.4, 1-nitropropylene 5.6, and 2-nitropropylene 1.6.

Activation energies were calculated for the competing unimolecular reaction, C-N bond fission, from thermochemistry and previously reported³ activation energies for the decomposition of 1,1- and 2,2-dinitropropane. Comparison of Arrhenius parameters for the two competing processes, namely, HONO and C-N bond fission, shows that, for the geminate dinitroethanes and dinitropropanes, C-N bond fission is faster above 370°K and, for the mononitroalkanes and for all the mononitroalkanes and dinitroalkanes, C-N bond fission is faster above 770°K.

Concerning the bis(difluoramino)alkanes, we earlier reported⁷ the results of experiments and RRK calculations on the decomposition of vibrationally excited 1,2-bis(difluoroamino)propane produced by the successive addition of NF₂ radicals to propylene. Dr. David Golden, the associate editor of the International Journal of Chemistry Kinetics, to whom we sent the manuscript for publication, pointed out that the assumptions we made in the calculation were valid for thermal activation but not for chemical activation, and that RRKM calculation would be needed. Dr. Golden and Dr. M. C. Lin of Naval Research Laboratory kindly assigned the frequencies and performed the RRKM calculation. A copy of the revised manuscript is given in the Appendix.

D. Detonation Failure: Variation of the Failure Diameter of Nitromethane with Temperature

From the theory of Dremin and Trofimov,⁸ the failure diameter of an unconfined cylindrical charge of an explosive liquid is given by

$$d_f = 2u_3 v \tau_3 a \quad (1)$$

where d_f is the failure diameter, u_3 is the particle velocity, v is the velocity of the quenching wave front perpendicular to the direction of detonation propagation, τ is induction time (smooth-shock reaction time),

and $a = [1/(D_3 - u_3)] + [1/(u_3 - c_3)]$, where D is the detonation velocity, c is the sound speed, and the subscript 3 refers to the regions of unreacted, shocked, explosive.

In a recent paper, Enig and Petrone⁹ calculated the failure diameter using equation (1) for nitromethane from 253.16° to 313.16°K and found good agreement with experiment. The objective of the present work was to find how each of the terms in equation (1) contributed to the variation in the failure diameter with initial, preshock, temperature, T_O .

On differentiating equation (1) with respect to T_O ,

$$\begin{aligned} \frac{ddf}{dT_O} &= 2v\tau_3 a \left(\frac{du_3}{dT_O} \right) + 2u_3\tau_3 a \left(\frac{dv}{dT_O} \right) + 2u_3va \left(\frac{d\tau_3}{dT_O} \right) + \\ &2u_3v\tau_3 \left\{ -\frac{1}{(D_3-u_3)^2} \frac{d(D_3-u_3)}{dT_O} - \frac{1}{(u_3-c_3)^2} \frac{d(u_3-c_3)}{dT_O} \right\} \\ &= A + B + C + D \end{aligned} \quad (2)$$

Enig and Petrone calculated d_f , τ_3 , u_3 , D_3 , and c_3 as a function of T_O for 10-degree intervals between 313.16 and 253.16°K. From their results, approximate values of the derivatives in equation (2) can be found. For example for $T_O = 313.16^\circ$ and 303.16° K, $d_f = 10.83$ and 14.05 mm, $\tau_3 = 0.116616$ and 0.157037 μsec^{-1} , $u_3 = 6.90291$ and 6.92923 mm μsec^{-1} , $D_3 = 8.40939$ and 8.5357 mm μsec^{-1} , and $c_3 = 5.57358$ and 5.7214 mm μsec^{-1} . (The velocity v is 4.75 mm μsec^{-1} and is temperature invariant.) That is, $dd_f/dT_O \sim -0.322$ mm deg^{-1} , of which the terms on the right-hand side of equation (2) contribute as follows: $A = 1\%$, $B = 0$, $C = -115\%$, and $D = 14\%$. Therefore by far the biggest contribution to the variation of failure diameter with initial temperature is the variation in induction time.

E. "Universal" Hugoniot for Liquids (with M. Cowperthwaite and R. W. Woolfolk)

In a previous report,¹ we developed a "universal" Hugoniot that improved the thermodynamic description of liquids in the 1-bar to 20-kbar region. Since then two experimental studies have been reported,^{10,11} The results, shown in Figure 4, tend to confirm the validity of the model.

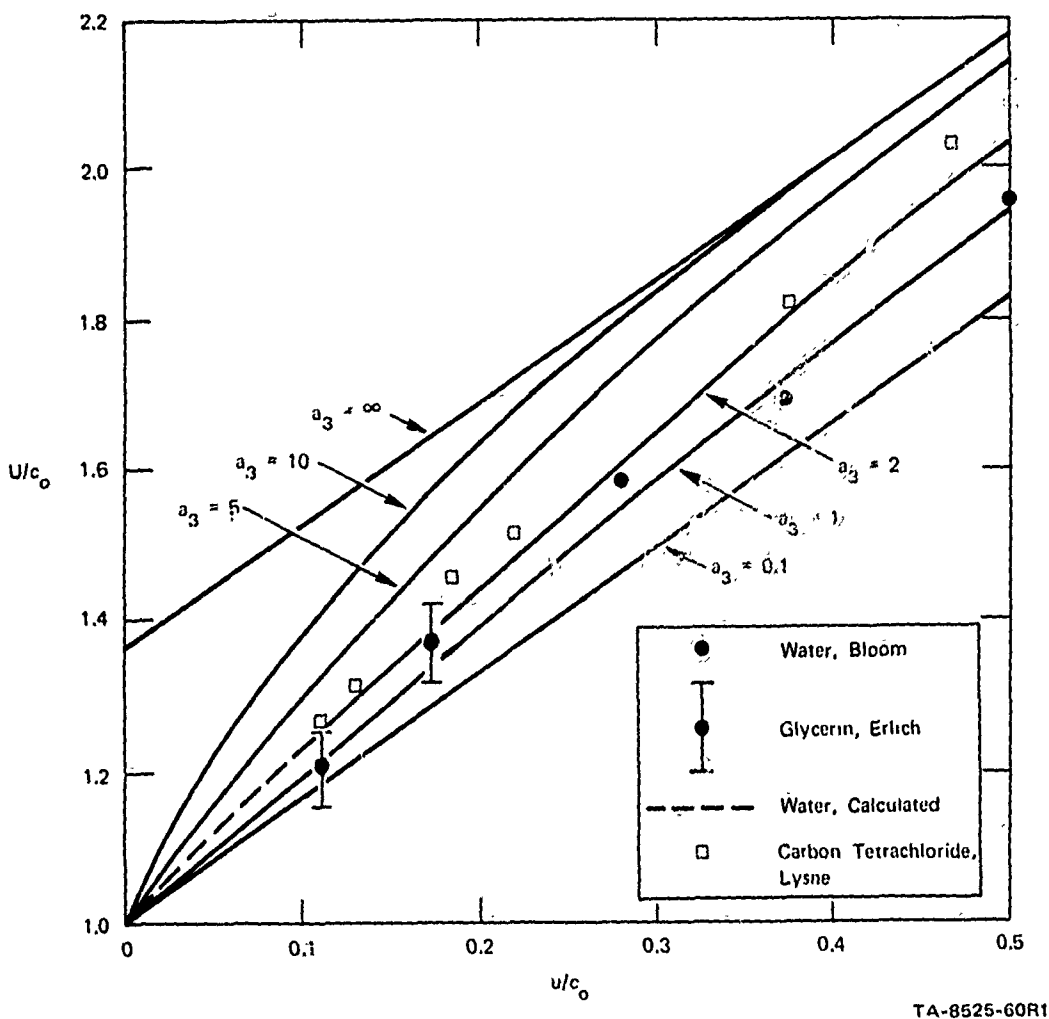


FIGURE 4 CALCULATED NORMALIZED U-u PLOTS FOR VALUES OF $a_3 = 0.1, 1, 2, 5, 10$, AND ∞ IN THE EQUATION $U/c_0 = 1.37 - 0.37 \exp [-a_3 u/c_0] + 1.62 u/c_0$ SHOWING ERICH'S EXPERIMENTAL GLYCERIN DATA, LYSNE'S EXPERIMENTAL CARBON TETRACHLORIDE DATA AND BLOOM'S EXPERIMENTAL DATA FOR WATER

F. Future Work

We are at present incorporating the "universal" Hugoniot described above into our model for shock temperature calculation. This is an important first step in testing Dremin's equation for failure diameter.

In connection with the shock initiation of liquid 2,2-DNP at 60°C, we plan to measure its lead-block failure diameter and to compare it with 1,1-DNP.

III LOW-VELOCITY DETONATION

(Robert Woolfolk)

A. Introduction

This portion of our overall program to relate sensitivity fundamentals to chemical structure concerns the occurrence of low-velocity detonations (LVD) in dinitroalkanes. These materials were chosen as model compounds for candidate monopropellants and energetic plasticizers. We are particularly interested in relating the chemical and physical properties of the dinitroalkanes to their LVD gap sensitivity.

A more complex phenomenon than conventional high order detonation, LVD is a reaction wave believed to be propagating in a cavitated medium. We believe that the formation of this cavitation and its relation to the container and the energetic liquid properties are important in LVD initiation and propagation.

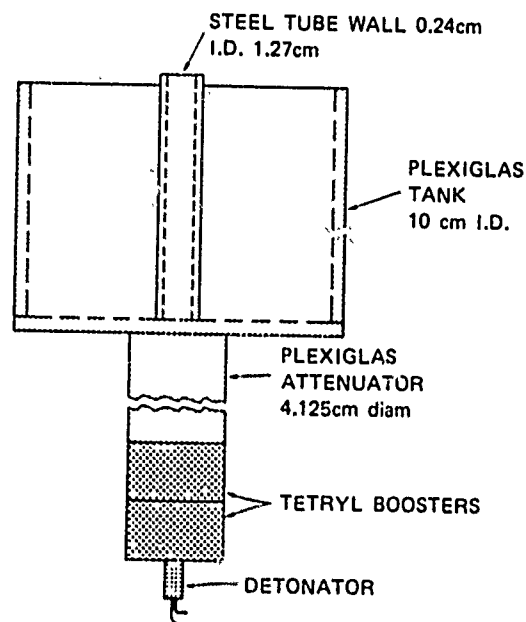
We have been studying the effect of temperature on the initiation of LVD using 1,1-DNE as a model compound. In addition we have determined the LVD gap sensitivity of the fluorine-substituted 1,1,1-FDNE and compared it with 1,1-DNE.

Pressure-time history studies during LVD initiation and propagation were conducted using FEFO. These results indicated the peak pressure and propagation velocities in LVD.

B. Experimental

We have conducted sensitivity gap tests to determine the temperature effects on the LVD gap sensitivity of 1,1-DNE. Using a modified version

of our LVD gap sensitivity test that enables us to conduct experiments at elevated temperatures, we determined both the HVD and LVD gap sensitivities for 1,1-DNE. Figure 5 shows a schematic of the test device. By placing hot water in the Plexiglas tank, we can maintain the temperature of the tube and its contents at a fairly constant temperature for the duration of the test. We chose to work near 60°C because we had previously studied the dinitropropanes at this temperature. Table III gives the results for the HVD gap sensitivity tests on 1,1-DNE.



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FIGURE 5 SCHEMATIC OF GAP TEST APPARATUS FOR ELEVATED TEMPERATURES

Table III

HVD GAP SENSITIVITY FOR 1,1-DNE

Plexiglas Gap (cm)	Witness Plate		Temperature (°C)
	+ go	- no go	
1.90 ^a		-	21
1.60 ^a		-	21
1.42		+	24
1.27 ^a		+	24
2.54		-	65
1.90		-	57
1.73		+	57
1.58		+	59

^a Results previously reported in reference 3.

The HVD gap sensitivity of 1,1-DNE under our test conditions is 1.42-1.60 cm of Plexiglas at 24°C and 1.73-1.90 cm at 57°C. As expected 1,1-DNE becomes more sensitive with increasing temperature.

The LVD test results are shown in Table IV. Because it was known from previous studies¹² that confinement has a major effect on the LVD gap sensitivity of some compounds, we determined the LVD gap sensitivity in a water-surrounded tube at ambient temperature so that a more reliable comparison could be made between the results at 60°C and 25°C. The LVD gap sensitivity of 1,1-DNE at 25°C is 7.00-7.60 cm and at 60°C, 6.35-7.00 cm of Plexiglas. These results are surprising in that the LVD sensitivity, at least for 1,1-DNE, decreases significantly as the temperature increases. This is in marked contrast to the HVD results and suggests that the initiation

mechanisms of these two process are quite different, as we previously found for the difluoroamino compounds.

Table IV

LVD GAP SENSITIVITY OF 1,1-DNE

Plexiglas Gap (cm)	Tube Surrounded by Water	Witness Plate		Temperature (°C)
		+ go	- no go	
7.60	Yes	-		25
7.00	Yes	+		25
6.35	Yes	+		25
16.0 ^a	No	-		18
8.25 ^a	No	-		24
6.35 ^a	No	+		24
4.30 ^a	No	+		25
10.8	Yes	-		59
8.25	Yes	-		58
7.60	Yes	-		60
7.00	Yes	-		62
6.35	Yes	+		59

^a Results previously reported in reference 3.

We also tested the fluorine-substituted dinitroethane, 1,1,1-FDNE, for HVD and LVD gap sensitivity. In these standard tests, consisting of a steel tube 1.27-cm i.d. with a 0.24-cm wall, HVD and LVD are detected by the use of witness plates, which are 0.63 cm thick for HVD and 0.16 cm for LVD. Each test is boosted by 100 g of tetryl, and the ensuing shock is attenuated by a Plexiglas attenuator. Results are shown in Table V.

Table V

HVD AND LVD GAP SENSITIVITY FOR 1,1,1-FDNE AT 24°C

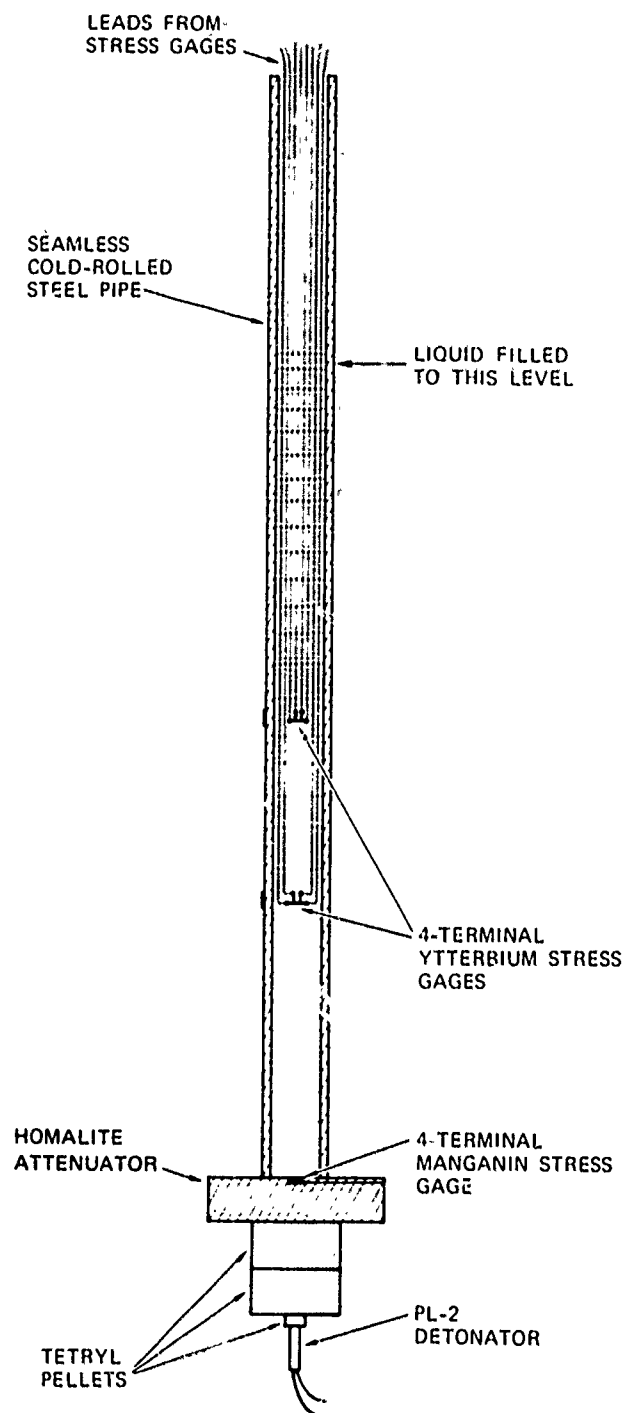
Plexiglas Gap (cm)		Witness Plate ^a + go - no go	
HVD	1.27	-	
	1.19	-	
	1.09	+	
	0.94	+	
	0.635	+	
LVD	8.25	-	
	7.00	+	
	5.71	+	

^a Witness plate is 0.63 cm thick for HVD,
0.16 cm for LVD.

The HVD gap sensitivity of 1,1,1-FDNE is 1.09-1.19 cm of Plexiglas, and the LVD gap sensitivity is 7.00-8.25 cm at 24°C. This makes 1,1,1-FDNE less sensitive than 1,1-DNE in the HVD gap sensitivity tests and about the same in the LVD test. Therefore the replacement of a hydrogen for a fluorine, at least for dinitroethane, reduces the HVD gap sensitivity and has little or no effect on the LVD sensitivity. HVD sensitivities of all of these DNP and DNE isomers are low, comparable to CH₃NO₂. LVD sensitivity of 1,1,1-FDNE is comparable to other dinitroalkanes which are low compared to difluoroaminoalkanes.

In collaboration with D. Erlich who is working on LVD and propagation at the Institute under the sponsorship of AFOSR (contract now expired), we performed several tests to measure the pressure-time history of a liquid during LVD initiation and propagation. These tests employ piezoresistive gages of manganin and ytterbium to measure stress levels in the initial input shock wave and subsequent waves that develop in the test liquid. This technique as used in these studies is fully described in Reference 13 and will be only generally described here. Figure 6 is a schematic diagram of the test procedure. Three gages were used to measure the stress: two ytterbium gages for the low levels of stress expected in the liquid and one manganin gage to measure the input pressure. We choose to study the liquid FEFO because its LVD sensitivity is greater than that of other liquids previously studied, such as ethyl nitrate. Table VI gives the initial condition for these tests and the pressure recorded at each gage station.

The initial stress entering the liquid was approximately 30 kbar and was subsequently reduced to below 10 kbar at the first gage even in the presence of LVD initiation. However, by the time the waves reached the second gage, the peak pressure in the LVD wave was at 4 kbar, and in Shot No. 6 where LVD was not initiated the stress decayed to 1.3 kbar. The propagation velocity for LVD in FEFO under these conditions appears to be about 3 mm/ μ sec. Similar studies on EN give a velocity of about 2 mm/ μ sec. The pressure-time history records in these shots was somewhat noisier than those seen previously for EN but were still good enough to give us an indication of the peak pressure in the initial wave. Further studies along these lines with 1,1-DNE may be attempted to obtain better pressure-time curves.



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FIGURE 6 SCHEMATIC DIAGRAM OF LVD EXPERIMENTS

Table VI

PRESSURE-TIME HISTORY EXPERIMENTS WITH FEFO

	Shot No. 6 ^a	Shot No. 7	Shot No. 8
Initial conditions			
Pipe i.d. (in.)	0.75	0.75	0.75
Pipe wall thickness (in.)	0.125	0.125	0.125
Pipe length (in.)	18	18	18
Height of liquid in tube (in.)	14	14	14
Thickness of homalite attenuator (in.)	1.03	1	1.53
Gages used			
Manganin gage in homalite	Yes		Yes
Ytterbium gage 1 - distance down pipe (in.)	4.5	4.5	4.5
Ytterbium gage 2 - distance down pipe (in.)	7.5	7.5	7.5
Results:			
Type of detonation initiated ^b	None	HVD	LVD
Peak liquid pressures measured,			
By manganin gage (kbar)	43		33
By ytterbium gage 1 (kbar)	c	c	7.3
By ytterbium gage 2 (kbar)	1.3	c	4.0
Propagation velocity of peak pressure seen by Ytterbium gages (mm/ μ sec)	c	c	2.97

^a Subsequent analysis of this FEFO batch showed that it contained 10-15% impurities.

^b As determined by terminal observation.

^c Data could not be analyzed.

C. Discussion

The effect of temperature on the gap sensitivity of 1,1-DNE can be divided into the HVD results and the LVD results. Table VII shows a summary of the results we have obtained to date on the dinitroalkanes.

Table VII

TEMPERATURE EFFECTS ON HVD GAP SENSITIVITY
OF 1,1-DNP AND 1,1-DNE

Compound	Temperature (°C)	Plexiglas Gap (cm)	Tube i.d. (cm)
1,1-DNP	15	1.02-1.09	1.27
1,1-DNP	60	1.40-1.52	1.27
1,1-DNE	23	1.42-1.60	1.27
1,1-DNE	60	1.73-1.90	1.27

We find that as the temperature is increased, the HVD gap sensitivity increases for both compounds. These results are in agreement with the reaction time studies discussed in Section II and in the last report.¹ The reaction time results show that increasing the initial temperature for 1,1-DNP decreases the reaction time at a given shock input (i.e., lowers the sensitivity). These results are expected because increasing the initial temperature will result in a higher final temperature and therefore faster reaction time for a given shock input pressure. When the effects of temperature on LVD gap sensitivity are examined, the results are not as expected.

Table IV shows that increasing the initial temperature actually decreases the LVD gap sensitivity of 1,1-DNE. Since this is the only

compound for which we have determined the LVD temperature effect, we cannot be sure if this is a general result or if it is peculiar to 1,1-DNE. (We had previously tried to study the LVD temperature effect using 1,1-DNP, but it did not undergo LVD at either ambient or elevated temperatures.) These results do suggest however, that the initiation mechanism for HVD and LVD are quite different. Chart I summarizes our results to date on the effects of temperature on the gap sensitivities of the dinitroalkanes.

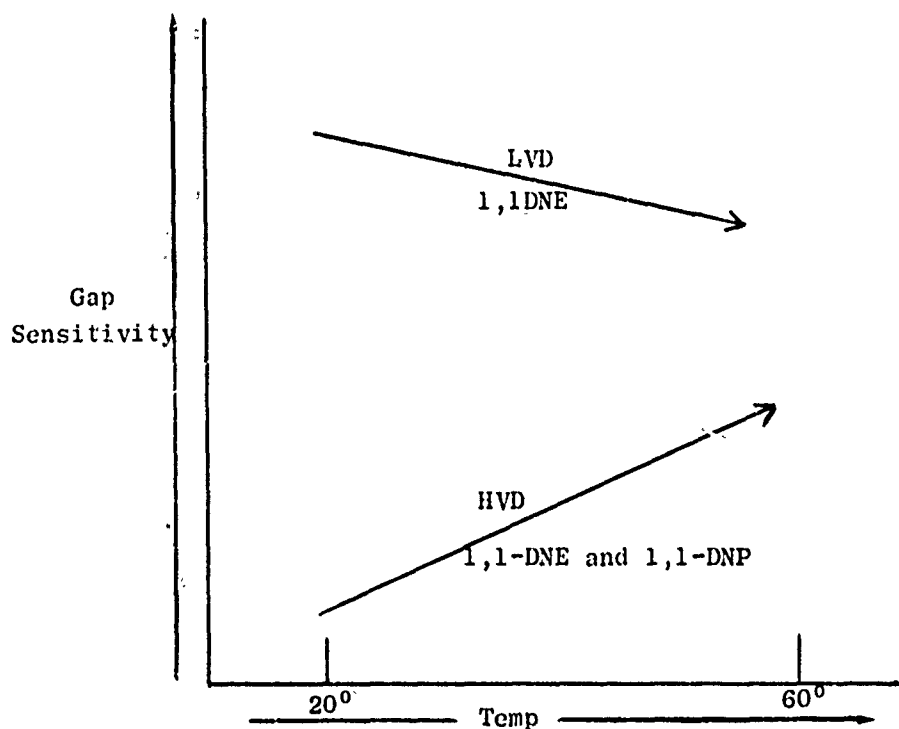


CHART I EFFECT OF TEMPERATURE ON GAP SENSITIVITIES OF DINITROALKANES

We had previously shown¹² for the difluoroaminoalkanes that the HVD and LVD initiation processes were different in that the order of sensitivity of 1,2- and 2,2-propane isomers was different for HVD and LVD.

A possible explanation for the temperature effects in 1,1-DNE could be related to the initial cavitation process whose temperature coefficient could be negative. The negative coefficient might be related to dissolved

foreign gases that act as cavitation centers when the liquid goes into tension under the dynamic shock interactions in these tests. At elevated temperatures the dissolved gases would be expelled, and there would then be fewer centers for cavitation. This would indicate that the controlling mechanism for LVD initiation is the production of cavitation. Further work is necessary to confirm this hypothesis. Such studies might include initiation of LVD in outgassed samples and the use of foreign gases with different heat capacities in initiation experiments.

We found that the HVD gap sensitivity of 1,1,1-FDNE was less than that of 1,1-DNE. This is also in agreement with the results from reaction-time measurements and may indicate the effects of the α -hydrogen in the initiation of HVD. However, the LVD gap sensitivity of the two dinitroethanes was the same. We had speculated that because FEFO (which contains a fluorodinitro group) was fairly sensitive to LVD initiation, 1,1,1-FDNE might be more sensitive than 1,1-DNP. TIGER calculation also indicated that there was less change in energy release with temperature in the fluorine-containing materials, and we felt that these materials might therefore exhibit a greater LVD gap sensitivity. This does not appear to be the situation.

In a previous report³ we suggested that the LVD gap sensitivity was related to oxygen balance. The latter was defined as the negative of the percentage of O_2 by weight required to oxidize a given weight of material to CO_2 and H_2O . Table VIII shows the oxygen balance of some materials and their LVD gap sensitivities. Although 1,1,1-FDNE has a low favorable oxygen balance, its LVD gap sensitivity is the same as that for 1,1-DNE, which has a much less favorable oxygen balance, and both EN and 1,1,1-FDNE are out of order in the table. Therefore it appears that oxygen balance is not a good criterion by which to estimate the LVD gap sensitivity.

Table VIII

OXYGEN BALANCE AND LVD GAP SENSITIVITY OF
SELECTED MATERIALS

Compounds	Oxygen Balance ^a	LVD Gap Sensitivity (cm)
2,2-DNP	-59.6	No LVD
1,1-DNP	-59.6	No LVD
1,1,1-FDNP	-42	b
NM	-39	No LVD
1,1-DNE	-26.5	7.00-7.60
2,2-DNE	-26.6	b
EN	-26.4	3.8-5.1
FEFO	-12.8	~11
1,1,1-FDNE	-11.6	7.0-8.25
1,1,1-Fluorodinitromethane	+25.8	b

^a Oxygen balance is defined as the negative percentage of O₂ by weight required to oxidize a given weight of material to CO₂ and H₂O.

^b To be tested when and if available.

In previous reports,^{1,12} we discussed the correlation of the LVD gap sensitivity and the ratio of the heat of reaction to the heat of vaporization ($\Delta H_r / \Delta H_v$). We have been using the TIGER code to calculate the ΔH_r for these materials, and we need next to determine ΔH_r for 1,1,1-FDNE and its heat of vaporization from vapor pressure measurements. However, on the basis of estimates of these values for 1,1,1-FDNP compared with 1,1-DNP and values for 1,1-DNP compared with 1,1-DNE, we can estimate

the value of $\Delta H_r / \Delta H_v$ as about 12.0. For comparison, Table IX lists the values for this parameter and the LVD gap sensitivity of several compounds. We can see that if $\Delta H_r / \Delta H_v$ is about 12.0 for 1,1,1-FDNE, then its LVD gap sensitivity fits the approximate ordering, where compounds with a large value of $\Delta H_r / \Delta H_v$ have greater LVD gap sensitivity. However, more data are needed to establish this type of correlation.

Table IX

LVD GAP SENSITIVITIES AND $\Delta H_r / \Delta H_v$ AT 2000°K AND
20 kbar FOR SELECTED COMPOUNDS

Compound	$\Delta H_r / \Delta H_v$	LVD Gap Sensitivity (cm Plexiglas)
NM	8.05	No LVD
1,1-DNP	10.9	No LVD
1,1-DNE	11.1	7.0-7.6 ^b or c
1,1,1-FDNE	12.0 ^a	7.0-8.3 ^b
EN	12.8	3.0-3.8 ^b or c
IBA	25.0	16-17 ^b or c
1,2-DP	21	30-40 ^b 91-127 ^c
2,2-DP	32.2	>180 ^c

^a Estimated value.

^b Without witness plate.

^c With witness plate.

It appears from the results of the pressure-time studies that the LVD wave develops a peak pressure of 5-10 kbar, which is in general agreement with previous estimates,¹⁴⁻¹⁶ although on the lower end of

these estimates. We feel that further experiments of this type would be useful on a material such as 1,1-DNE, which is not too sensitive, to see if the pressure within the wave is a function of sensitivity and wave velocity. Previous studies¹³ on EN and FEFO have indicated that the velocity is higher in a more sensitive liquid and that the peak pressure also appears somewhat higher in FEFO than in EN. Strain gages on the tube wall should also indicate how pressure waves interact with the liquid to produce the cavitation believed to have such an important effect on LVD initiation and propagation.

D. Future Work

Our future work on LVD initiation and chemical structure will concentrate on mixtures of 1,1-DNE, which undergoes LVD, and 1,1-DNP, which does not. These studies will attempt to determine the critical energy mixture that will just propagate LVD. From these studies we hope to ascertain whether the concept of a minimum energy for LVD initiation has validity. TIGER code will be used to estimate the energy of the mixtures. Physical parameters such as vapor pressure and viscosity will also be measured for comparison with the LVD gap sensitivities.

To continue our studies of the effects of fluorine substitution, we will determine the HVD and LVD gap sensitivities of 1,1,1-fluoro-dinitroethanol, whose structure is between 1,1,1-FDNP and FEFO. Since the last two have quite different LVD gap sensitivities, the dinitroethanol study should prove enlightening.

Pressure-time studies may continue, using 1,1-DNE to check the peak pressure and wave velocity for this material and to attempt better correlation between the wall wave and LVD initiation and propagation.

IV STATIC HIGH-PRESSURE EXPERIMENTS

(David S. Ross)

A. Introduction

The static high-pressure experiments on dinitroalkanes have shown that the compounds display an α -hydrogen effect under these conditions, similar to that observed in the smooth-shock reaction time experiments.¹ Thus compounds with α -hydrogens, such as 1,1-DNP and 1,2-DNP, at a given temperature and pressure have a shorter time to explosion than those without an α -hydrogen, such as 2,2-DNP and 1,1,1-FDNP. Moreover, for 2,2-DNP a pressure increase lengthens the time to explosion, whereas for 1,2-DNP and 1,1-DNP a pressure increase shortens the time to explosion. Clearly, there are some factors dependent on the structure of the specific sensitive liquid that affect the overall shock sensitivity of the materials. It is of interest therefore to gain some additional insight into the critical molecular processes taking place during the initiation period. For this purpose we have designed a system for measuring gross rates of reactions and initial products formed during the initiation period at pressures and temperatures comparable to those encountered in shock initiation experiments.

B. One-Atmosphere Runs

Initially we carried out several experiments with 40- μ l (370- μ mole) samples of 1,1-DNP at 1 atm in glass break-seal tubes to calibrate the analytical technique and to serve as a reference point for the high-pressure experiments. In experiments at 155°C for 39 hours, 1,1-DNP decomposed to the extent of 1 to 3%. This conversion was about 20 times

greater than that calculated from the gas-phase unimolecular rate parameters¹ and suggests that some secondary reaction takes place, with possible incursion of autocatalysis or a free radical chain as well. Product analyses are shown in Table X.

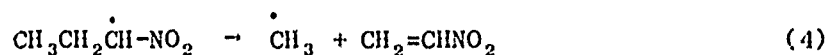
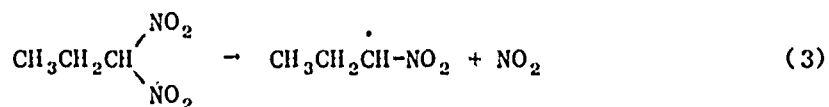
Table X

DECOMPOSITION OF 1,1-DNP AT 155°C AND 1 ATM PRESSURE

Product	Amount (μmoles)
N ₂	2.4
N ₂ O	19.0
CO ₂	12.5
CH ₄	tr
C ₂ H ₆	tr
CO	tr
CH ₃ NO ₂	~12
Unknown	~12

Formation of N₂, N₂O and CO₂ are not unexpected products if NO₂, produced by initial scission at the C-N bond, is acting as an oxidizing agent.

Formation of CH₃NO₂ is consistent with a scheme in which nitropropyl radical undergoes β-scission.



It is possible but unlikely that the unidentified product is nitroethylene formed in Step (4) since that olefin is probably unstable and is not expected to survive the reaction conditions.

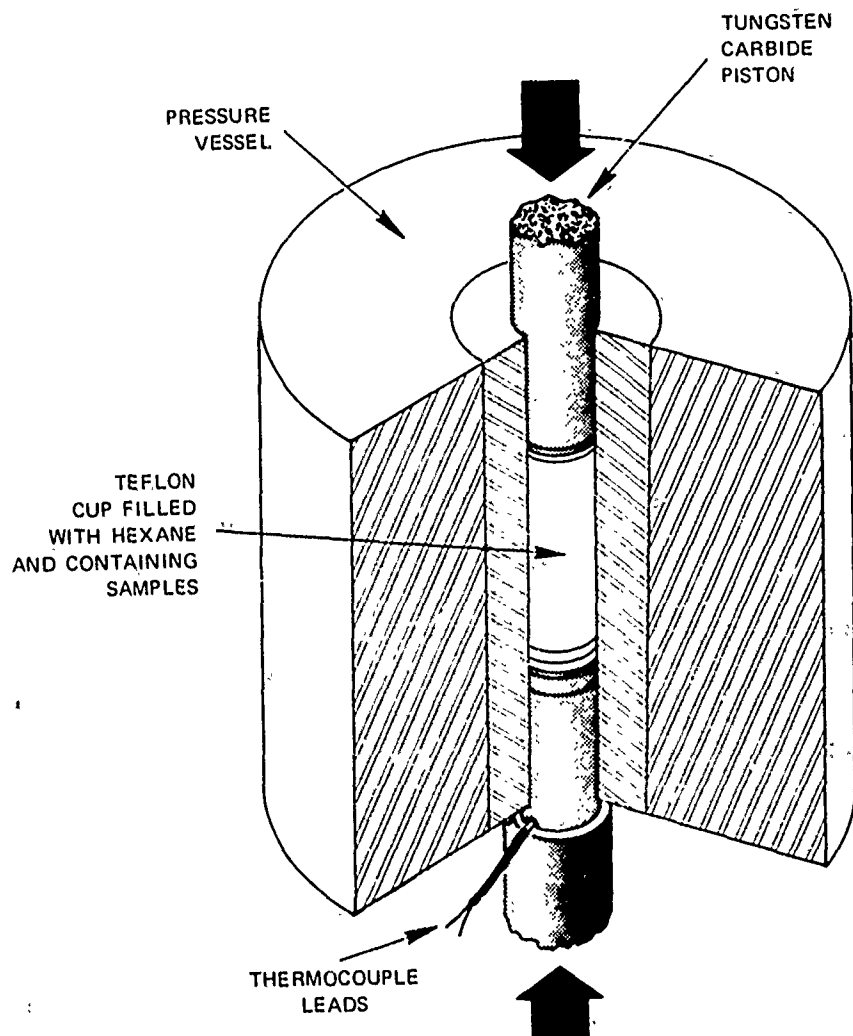
Reactions (3) and possibly (4) were both observed in our very low-pressure pyrolysis (VLPP) experiments with 1,1-DNP.¹ The subsequent recombination (5) would be expected to occur under the condensed phase conditions. Other radical reactions, such as hydrogen abstractions by CH_3 and possibly NO_2 , are apparently not important under these conditions.

C. High-Pressure Runs

The high-pressure experiments were run in an assembly similar to that described in an earlier report.⁷ We used a conventional piston-cylinder apparatus, shown in Figure 7, wrapped with a heating tape, and holding a snugly fitting Teflon cup. The cup is filled with hexane, which serves well as both a pressure and temperature transmitting medium. Forty- μl samples of liquid are sealed in No. 20 Teflon "spaghetti" tubing (see below). The Teflon cup can accommodate several of these sample tubes. The pressure is applied by means of a conventional hydraulic pump, and after the reactor is brought to pressure, the entire assembly is heated for some appropriate period. At the end of a run, the system is cooled to room temperature, and then the pressure is released.

The products are isolated by cutting the tubing open in a vacuum system and transferring the volatile materials to various analytical stations, including gas chromatography and infrared and mass spectrometry. The relatively nonvolatile materials are removed from the system and analyzed by gas chromatography.

The critical feature of high-pressure experiments, not yet entirely resolved is the design of a suitable seal for the tubing that will retain gases on release of pressure. In our first experiments with 1,1-DNP,



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FIGURE 7 HIGH PRESSURE ASSEMBLY

the tubing was sealed by folding over the ends of the Teflon tubing, sliding snugly fitting short lengths of metal tubing over the doubled ends, and then crimping the metal firmly. However, this type of seal proved inadequate; in the first high-pressure experiments (run for 42 hours at 150°C and 1.8 kbar), release of pressure led to evolution and loss of a large volume of gas. Moreover the liquid within the sample

tubes contained some dark brown particulates, which might have been the end result of homogeneous decomposition of 1,1-DNP under the prevailing conditions. However, we cannot rule out the possibility of the interaction of 1,1-DNP with some material on the surface of the tubing such as an extrusion lubricant. (We had been informed by the supplier of the tubing that the material was free of any filler or surface additive.)

With these reservations in mind, we found the product analysis for this run interesting. First, there are two major products formed, as of now unidentified, which were absent in the one-atmosphere runs. They are relatively volatile, and should they occur in a repeat run using "clean" tubing, they will be identified.

Second, no nitromethane was present in this run. Thus there are clearly differences between gas-phase and low and high pressure liquid-phase runs. These preliminary results are encouraging, providing for the first time information about changes in products and rates over a pressure range of about 10^9 on going from VLPP to 1.8 kbar.

D. Future Work

The sealing difficulties described above are minor, and we expect to develop a satisfactory procedure very soon. Additional experiments in clean containers are now in progress, and the major products from decomposition of 1,1-DNP at high pressure should be identified shortly. We plan next to examine the decomposition of 2,2-DNP to compare the variation in overall rates with pressure to changes in smooth-shock reaction times.

V PUBLICATIONS

The following papers have been submitted or accepted for publication during this report period:

"The Kinetics of Unimolecular Dehydrofluorination of 1,2-Bis(difluoramino)propane," D. S. Ross, R. Shaw, and D. M. Golden (SRI) and M. C. Lin (Naval Research Laboratories), International Journal of Chemical Kinetics, submitted.

"Heats of Formation and Kinetics of Decomposition of Nitroalkanes," R. Shaw, International Journal of Chemical Kinetics, accepted.

"A Universal Hugoniot for Liquids," R. W. Woolfolk, M. Cowperthwaite, and R. Shaw, Thermochnica Acta, accepted.

"Shock Initiation of Liquid Nitromethane and Methyl Nitrite," R. Shaw, Journal of Chemical Physics, submitted.

"Very Low Pressure Pyrolysis of Dinitropropanes", D. S. Ross and L. Piszewicz, J. Am. Chem. Soc., submitted.

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14. R. W. Woolfolk and A. B. Amster, "Low Velocity Detonations: Some Experimental Studies and Their Interpretation," Twelfth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh (1969) p. 731.
15. R. W. Watson, C. R. Summers, F. C. Gibson, and R. W. Van Dolah, "Detonations in Liquid Explosives--The Low Velocity Regime," Proceedings, Fourth Symposium (International) on Detonation, ACR-126, Office of Naval Research, Department of the Navy, Washington, D. C., p. 117.
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Appendix

THE KINETICS OF THE UNIMOLECULAR DEHYDROFLUORINATION OF 1,2-BIS(DIFLUORAMINO)PROPANE

by

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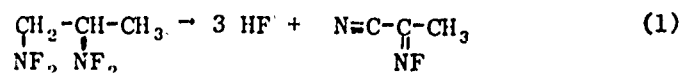
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SUMMARY

Vibrationally excited 1,2-bis(difluoramino)propane (1,2-DP) was produced from the reaction of propylene with N_2F_4 at $135^\circ C$. At 2 torr, the lowest pressure studied, more than 98% of the "hot" 1,2-DP was stabilized. The remaining molecules lost 3 moles of HF to form the imino-nitrile, $NCC(NF)CH_3$. Thus at $135^\circ C$, $k_{elim} = 10^{5.5} \text{ sec}^{-1}$. RRKM theory was used to calculate an activation energy of 38.0 kcal/mole for the loss of HF from 1,2-DP, using an A-factor of $10^{13.1} \text{ sec}^{-1}$. There is little difference between the above Arrhenius parameters and those reported previously for the loss of HF from methyldifluoramine.

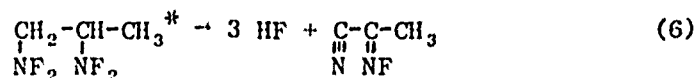
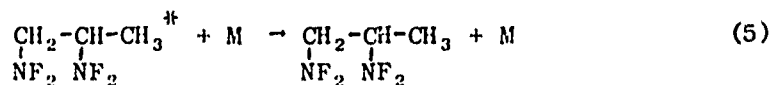
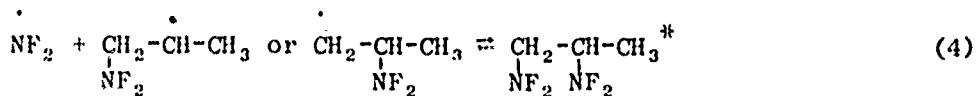
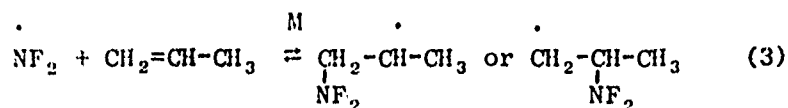
1. INTRODUCTION

The object of this work was to determine the activation energy for the unimolecular elimination of HF from 1,2-bis(difluoramino)propane (1,2-DP).



This reaction study represents an extension of our earlier kinetic studies of unimolecular HF elimination from CH_3NF_2 [1,2], ($E = 42$ and 38 kcal/mole, respectively), and is significant to the thermal explosion of 1,2-DP [3].

Direct observation of the HF elimination was masked by surface catalyzed decomposition at lower temperatures, and by the competing unimolecular C-N bond scission at higher temperatures [4]. This problem is avoided by making vibrationally hot 1,2-DP from the successive addition of two NF_2 radicals to propylene [5]. The reaction sequence is then (an asterisk denotes a vibrationally excited species):



2. EXPERIMENTAL

The experimental arrangement was that used previously [1], except that the gas chromatograph was modified to take a sample directly from the reaction vessel without having to condense the reaction mixture. No inert diluents were added and the temperature of the reaction vessel was 135°C. To confirm the retention time, some imine was prepared by the reaction of 1,2-DP with pyridine [6].

3. RESULTS AND DISCUSSION

In the analogous CH_3NF_2^* system, the ratio of yield of stabilized difluoraminoalkane to the yield of HCN was observed to be a linear function of M up to 10 atmospheres pressure. In the present study, it was not possible to verify the linear effect of pressure because most of the hot 1,2-DP was stabilized even at 2 torr, the lowest pressure that could be reasonably studied. From the trace of imine observed at 2 torr, the ratio of imine to stabilized 1,2-DP was 1 to 64. The collision frequency (k_g) was taken to be $10^7 \text{ torr}^{-1} \text{ sec}^{-1}$, and every collision was assumed to have unit efficiency; that is, $k_g/k_s [M] = 1/64$, from which we obtain $k_g = 10^{5.5} \text{ sec}^{-1}$.

For the 1,2-DP molecule, the following frequencies, in cm^{-1} , and degeneracies were assigned: 3000 6, 1460 3, 1340 4, 1280 1, 1170 1, 1100 4, 990 3, 860 2, 750 1, 560 2, 415 6, 350 2, 200 1, 30 3. The entropy, in cal/(mole-K), of the 1,2-DP molecule was made up of:

Translation	40.8773
Vibrational	29.9522
External rotation	30.9069
Total entropy	101.7364

For the transition state for unimolecular decomposition of 1,2-DP the assigned frequencies, in cm^{-1} , were: 3000 5, 2200 2, 1460 3, 1355 2, 1280 1, 1170 1, 1100 3, 990 3, 860 1, 750 1, 690 2, 520 3, 420 4, 315 3, 200 1, 130 1, 30 2. The entropy, in $\text{cal}/(\text{mole-K})$, of the activated complex consisted of:

Translation	40.8773
Vibration	28.0068
External rotation	32.2843
Total entropy	101.1684

The entropy difference between the initial state and the transition state corresponded to an Arrhenius A-factor of $10^{13.1} \text{ sec}^{-1}$.

For the RRKM calculation, the frequencies, in cm^{-1} , and degeneracies of the activated complex were simplified to: 3000 5, 2200 2, 1393 6, 1033 8, 524 10, 241 5, and 30 2. The C-N bond strength was taken to be 59.5 kcal/mole [1,2].

The RRKM calculation gives a calculated k_5 for different input activation energies at 0°K . The values of k_5 (at 2 torr pressure) in sec^{-1} , at the corresponding activation energies at 300°K , in kcal/mole , are: $10^{6.4}$ 36.6, $10^{5.3}$ 38.6, and $10^{4.2}$ 42.6. Interpolating the experimentally observed value for k_5 of $10^{5.5} \text{ sec}^{-1}$ gives an activation energy of 38.0 kcal/mole .

The rate constant for the unimolecular elimination of HF from 1,2-DP is therefore given by $\log (k/\text{sec}^{-1}) = 13.1 - 38.0/\theta$, where θ is $2.3 RT$ kcal/mole . This is very similar to the rate constant calculated using essentially the same program for the unimolecular elimination of HF from methyl difluoramine [2]; namely, $\log (k/\text{sec}^{-1}) = 13.5 - 38/\theta$.

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